

SeD Radical: A probe for measurement of time variation of Fine Structure Constant(α) and Proton to Electron Mass Ratio(μ)

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Based on the spectroscopic constants derived from highly accurate potential energy surfaces, the SeD radical is identified as a spectroscopic probe for measuring spatial and temporal variation of fundamental physical constants such as the fine-structure constant (denoted as $\alpha = \frac{e^2}{\hbar c}$) and the proton-to-electron mass ratio (denoted as $\mu = \frac{m_p}{m_e}$). The ground state of SeD ($X^2\Pi$), due to spin-orbit coupling, splits into two fine structure multiplets $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. The potential energy surfaces of these spin-orbit components are derived from a state of the art electronic structure method, MRCI+Q inclusive of scalar relativistic effects with the spin-orbit effects accounted through the Breit-Pauli operator. The relevant spectroscopic data are evaluated using Murrell-Sorbie fit to the potential energy surfaces. The spin-orbit splitting (ω_f) between the two multiplets is similar in magnitude with the harmonic frequency (ω_e) of the diatomic molecule. The amplification factor (K) derived from this theoretical method for this particular molecule can be as large as 350, on the lower side it can be about 34. The significantly large values of K indicate that SeD radical can be a plausible experimental candidate for measuring variation in α and μ .

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I. INTRODUCTION

Spatial and temporal variation of the fundamental constants to some level points to the invalidation of the Einstein's equivalence principle[1, 2]. These include the coupling constant of electromagnetic interaction, usually called as fine-structure constant (denoted as $\alpha = \frac{e^2}{\hbar c}$) and the proton-to-electron mass ratio (denoted as $\mu = \frac{m_p}{m_e}$). Over vast space and large time scale of the expanding universe these variations can be astrophysically measured and compared to the high precision laboratory data[3]. Recent advances in computational methods and high-precision experimental techniques propelled researchers to propose different experiments as well as experimental candidates aimed at the determination of such variation in the last few decades[4, 5]. High precision trapped atom and molecular ion spectroscopy is one of the most promising approaches for measuring such space-time variation of the fundamental physical constants experimentally, as molecular spectroscopy is sensitive to both the dimensionless constants α and μ [6, 7]. These spectroscopic techniques employ a diatomic molecule as a probe for measuring such variations in fundamental physical constants following the proposal put forward by Flambaum and Kozlov[8].

Diatomic molecules or radical having nearly degenerate long lived rotational and vibrational levels belonging to different electronic states are particularly sensitive to measure the variation in α and μ due to several orders of magnitude enhancement[8]. In case of a neutral or charged diatomic molecule having unpaired electrons with ground state fine structure multiplet the transition

frequency between the two multiplet states is given by,

$$\omega = \omega_f - v\omega_e; \quad v = 1, 2, 3, 4, .. \quad (1)$$

where ω_f is the magnitude of spacing between the multiplets (spin-orbit), ω_e is the magnitude of vibrational spacing under harmonic approximation and v is the vibrational quantum number[8]. The fine structure interval ω_f holds the relation with α as $\omega_f \sim Z^2\alpha^2 E_H$, where Z is the nuclear charge and $E_H = \frac{m_e e^4}{\hbar^2}$. On the other hand ω_e is related to μ which is given by $\omega_e \sim M_r^{-\frac{1}{2}} \mu^{-\frac{1}{2}} E_H$. Therefore ω is sensitive to the variation of both α and μ as given by the following equations,

$$\delta\omega = 2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_e \frac{\delta\mu}{\mu} \quad (2)$$

On the other hand the fractional variation of ω may be written as[8]

$$\begin{aligned} \frac{\delta\omega}{\omega} &= \frac{1}{\omega} (2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_e \frac{\delta\mu}{\mu}), \\ &= 2K \left(\frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right), \end{aligned} \quad (3)$$

where $K = \frac{\omega_f}{\omega_f - v\omega_e} = \frac{\omega_f}{\omega}$ [8] is known as the enhancement factor or the amplification factor. According to Flambaum and Kozlov large value for K of a species hints at its potential candidature as an experimental probe to gauge the variation in α and μ . Ideally diatomic molecules for which $\omega = 0$ would be the best possible probes for such purpose. However it turns out

that such a possibility is purely fortuitous as no such diatomic molecules exist. This limits the search for such diatomic molecules to cases where $\frac{\omega_e}{\omega_e}$ and K is substantially large. Unfortunately there are very few molecules which obey this criterion. Therefore it is essential to identify molecular candidates on which both experiments can be performed and astrophysical observations can be made. Flambaum *et.al.* and others have recently proposed certain candidates as viable probes, such as Cs_2 [9], MgH , CaH^+ [10, 11], Cl_2^+ , IrC , HfF^+ [13, 14], NH^+ [15–17], SiBr [18]. Out of these few do not have permanent dipole moments and are inactive to microwave spectroscopy. Although SiBr is relevant but its harmonic stretching frequency falls out of the infrared spectroscopy window. It is imperative to identify new candidates as this would enrich the gamut of probes so that more systematic analysis can be conducted. In this paper we identify Selenium Deuteride (SeD) as a potential candidate for experimentally probing the variation of fundamental physical constants and perform detailed theoretical study on that particular molecule to find variation in transition frequency upon a given change in α and μ . Although NH_3 and other C-H compounds are astrophysically abundant, SeD radical is yet to be observed. However, Asymptotic Giant Branch stars are probable sites to look for SeD due to the abundance of s-process isotopes and freely available deuterium in the cooler portion of the universe. The added advantage would be the cooler temperature for good IR observation which can be potentially important complementarity to the microwave observations made on NH_3 inversion. Laboratory experiment wise SeD is very similar to the trapping of NH or CaH molecules in magneto-optical traps[2, 19] and hence it may be considered as a possible candidate for fundamental test. Chemically, SeD is an open shell molecule with one unpaired electron ($S = \frac{1}{2}$) in its π orbital with a π^3 configuration. The first excited state $A^2\Sigma^+$ is well separated (about $30,460\text{cm}^{-1}$) with the ground state $X^2\Pi$. For linear molecule under spin-orbit coupling (SOC) the electronic states can be expressed as $\Omega = |\Lambda + \Sigma|$, where, Λ and Σ are the orbital and spin angular momentum. Under SOC splitting the $X^2\Pi$ state will split into $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ for $\Lambda = 1, \Sigma = \pm\frac{1}{2}$ and there is no split for $A^2\Sigma^+$ because of $\Lambda = 0, \Sigma = \frac{1}{2}$. According to the Hund's rule for more than half filled (π^3 electronic configuration) $^2\Pi_{\frac{3}{2}}$ is energetically lower than $^2\Pi_{\frac{1}{2}}$. The fine structure and vibrational spacings of the $X^2\Pi$ state are similar in magnitude ($\omega_f \approx v\omega_e, v = 1$)[20].

II. RO-VIBRONIC ENERGY LEVELS IN SELENIUM DEUTERIDE

The total Hamiltonian can be expressed as,

$$H = H_{Vib} + H_{SO} + H_{Rot} \quad (4)$$

for a $^2\Pi$ state the terms on the right hand side of the equation represents vibronic Hamiltonian, spin-orbit interaction Hamiltonian and rotational Hamiltonian respectively. The vibronic energy (in cm^{-1}) of a given electronic state in an anharmonic oscillator approximation taking upto first order term in $(v + \frac{1}{2})$ is,

$$E_{Vib}(v) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e\chi_e \quad (5)$$

where ω_e and $\omega_e\chi_e$ are harmonic vibrational frequency and first correction due to anharmonicity respectively. Now, for the case of spin-orbit interaction the orbital angular momentum (\vec{L}) and spin angular momentum (\vec{S}) are strongly coupled to the internuclear axis. If we denote the axial component of \vec{L} and \vec{S} as Λ and Σ the spin-orbit coupling Hamiltonian will be,

$$H_{SO} = A_v\Lambda.\Sigma \quad (6)$$

where A_v is the spin-orbit coupling constant. A_v depends on the vibrational quantum number as per the following relation derived by Brown and co-workers[21] (expanded upto the first order of $(v + \frac{1}{2})$ term)

$$A_v = A_e\alpha_{A_e}(v + \frac{1}{2}) \quad (7)$$

Therefore the spin-orbit Hamiltonian becomes,

$$H_{SO} = A_e\Lambda\Sigma - \alpha_{A_e}(v + \frac{1}{2})\Lambda\Sigma \quad (8)$$

In a molecular system rotation, vibration and electronic interactions influence one another. For the rovibrational electronic spectra of a diatomic molecule, the different angular momenta, i.e. electron spin angular momentum (\vec{S}), electron orbital angular momentum (\vec{L}) and angular momentum of nuclear rotation (\vec{R}) can couple in various ways to form the resultant angular momentum \vec{J} . These type of coupling are described by Hunds coupling cases. The ground state electronic multiplet, $X^2\Pi$, of SeD falls into the category of Hunds case (a) type of diatomic molecule where electronic orbital angular momentum \vec{L} is weakly coupled with the nuclear rotation and strongly coupled with the inter nuclear axis by electrostatic force i.e. $|\frac{A_e}{B_e}| \ll 1$. Spin angular momentum (\vec{S}) is strongly coupled to orbital angular momentum (\vec{L}) by spin orbit coupling. The electronic angular momentum for a rotating diatomic molecule is defined as $\Omega = \Lambda + \Sigma$ (Where Λ and Σ are the axial components of \vec{L} and \vec{S}). Angular momentum of the rotating nuclei (\vec{R}) is coupled to Ω to form total angular momentum $\vec{J} = \Omega + R$. After neglecting the centrifugal force terms the rotational energy in Hunds case (a)[22], rotational Hamiltonian will be that of asymmetric top with Ω as the angular momentum about the internuclear axis. The effective Hamiltonian in case for Hunds case (a) is

$$H_{Rot} = |B_v|R^2 \quad (9)$$

where B_v is the rotational constant. Hunds case (a) is a good representation when $A_e\Lambda$ is much greater than B_vJ , where A_e is the spin-orbit coupling constant. The rotational energy is given by,

$$E_{Rot}(J) = B_v[J(J+1) - \Omega^2] \quad (10)$$

B_v is dependent on the vibrational quantum number v . Expanding the rotational constant upto the first order of $(v + \frac{1}{2})$ term, where α_e is rotation-vibration coupling constant

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) \quad (11)$$

Therefore the final form of the rotational energy can be written as,

$$E_{Rot}(J) = B_e[J(J+1) - \Omega^2] - \alpha_e[J(J+1) - \Omega^2](v + \frac{1}{2}) \quad (12)$$

Now, since the spin-orbit coupling and the vibronic energy are large compared to the rotational energy, the total energy of the Hamiltonian will clearly be the sum of the individual energies and can be expanded in terms of spectroscopic constants by,

$$E(v, J) = \pm [A_e - \alpha_{A_e}(v + \frac{1}{2})] + (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x_e + B_e[J(J+1) - \Omega^2] - \alpha_e[J(J+1) - \Omega^2](v + \frac{1}{2}). \quad (13)$$

Here the top and bottom sign denotes the $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ state respectively. α_{A_e} may be represented as the difference of the harmonic frequencies of $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ state when considered independently[21]. The total energy can be separated into the summation of J dependent and the J independent part,

$$E(v, J) = G(v) + F_v(J) \quad (14)$$

where,

$$G(v) = \pm \frac{1}{2}A_e - B_e\Omega^2 + (\omega_e \mp \frac{1}{2}\alpha_{A_e} + \alpha_{A_e}\Omega^2)(v + \frac{1}{2}) - (v + \frac{1}{2})^2\omega_e x_e \quad (15)$$

$$F_v(J) = B_e[J(J+1)] - \alpha_e[J(J+1)](v + \frac{1}{2}) \quad (16)$$

Separating the energy in terms of J dependency allows us to pick up vibrational levels belonging to different spin-orbit coupled electronic states having similar energy. As a further refinement to the energy level difference, J 's belonging to same or different vibrational levels can be chosen as per the experimental requirements.

III. COMPUTATIONAL DETAILS

The ground electronic state $X^2\Pi$ of Selenium Deuteride radical is thoroughly studied in this paper. The ground state electronic configuration of $X^2\Pi$ SeD is $(3s_{Se})^2(3p_{zSe} + 1s_H)^2(3p_{\pi Se})^2(3p_{\pi Se})^1$. If one electron is transferred from $(3p_{zSe} + 1s_H)$ orbital to $(3p_{\pi Se})$ the first excited state $^2\Sigma^+$ is formed with the configuration $(3s_{Se})^2(3p_{zSe} + 1s_H)^2(3p_{\pi Se})^2(3p_{\pi Se})^2$. The theoretical characterization of potential energy curves for the ground state and the first excited state over an extended inter nuclear separation until dissociation requires the account of both static and dynamic correlation effects. In this study for the ground state, these effects has been included by the use of state-averaged complete active space SCF(SA-CASSCF)[23, 24] calculation on each doublet spin symmetry followed by single and double electron excitation on top of the zeroth order multi reference wavefunction (MRCISD). SA-CASSCF step involved the two states of symmetry $B_1(\Pi_x)$ and $B_2(\Pi_y)$ in the C_{2V} point group representation, the symmetries in the parenthesis are the corresponding one in the $C_{\infty V}$ point group. The active space consists the distribution of 7 electrons over 5 orbitals(CAS(7,5)). Since single and double electron excitation on top of CAS wave function is computationally very demanding, so Configuration State Function(CSF) with coefficients greater than 0.01 only are included to construct the new zero-order CI space. A further reduction of the dimension of the CI wavefunction has been made with internally contracted configuration interaction (IC-MRCISD) approach[25, 26] by restricting the core occupation to $(7A_1, 3B_1, 3B_2, 1A_2)$ where A and B denotes the symmetries of the irreducible representation in C_{2V} point group symmetry.

The molecular orbitals constructing the CSF's are the natural orbitals which are obtained by diagonalization of state-averaged (B_1 and B_2 state in C_{2V} point group symmetry) density matrix. Douglas-Kroll contracted correlation consistent Dunning's VnZ-DK(n=3-5)[27, 28] basis sets, employed for both the atoms, used in the expansion of natural orbital. The second-order Douglas-Kroll-Hess Hamiltonian has been used for all MRCI and CASSCF computations to account for the scalar relativistic effects[29, 30].

In the next step, the major focus is to determine the spin-orbit coupling. Technically spin-orbit contribution is computed using two steps: first, the SO Hamiltonian is added in a fashion of general first order perturbation procedure to the electronic Hamiltonian to construct the total Hamiltonian of the form $\hat{H} = \hat{H}_{el} + \hat{H}_{SO}$. The spin-orbit matrix elements \hat{H}_{SO} are calculated between the internal configurations (i.e. no electron in the external orbitals) $^2\Pi(^2B_1)$ and $^2\Pi(^2B_2)$ with the spin-orbit full

Breit-Pauli(BP)[31] operator of the form

$$\hat{H}_{SO} = \frac{1}{2m^2c^2} \left[\sum_i \sum_{\alpha} \frac{Z_{\alpha}e^2}{r_{i\alpha}^3} \hat{I}_{i\alpha} \cdot \hat{S}_i - \sum_i \sum_{\alpha} \frac{e^2}{r_{ij}^3} \hat{I}_{ij} \cdot (\hat{S}_i + 2\hat{S}_j) \right] \quad (17)$$

which contains both one and two electron terms. Here \hat{I} and \hat{S} are orbital and spin angular momentum operators, i and α denotes electron and nucleus respectively.

In the next step, $\hat{H} = \hat{H}_{el} + \hat{H}_{SO}$ matrix is diagonalised in the basis of SA-CASSCF/IC-MRCISD(7,5) wavefunctions to yield the desired spin-orbit splitting directly.

In order to improve the level of description this spin-orbit splitting is added as *a posteriori* correction to the corresponding MRCI+Q energy at each internuclear separation, where +Q denotes the quadruple excitation corrected by Davidsons method[32, 33]. These calculations have been carried out with the MOLPRO[34] suite of programs.

IV. THE POTENTIAL ENERGY FUNCTION

Among the functions that was proposed to fit the Analytical Potential Energy Functions(APEF) of diatomic molecules, Murrel Sorbie (MS) potential energy function seems to be the best one[35–40]. The interaction potential energies of many neutral and cationic diatomic molecules can be accurately reproduced by this function and has been used to deduce APEFs for many molecules[35–40]. The general form of MS function is given by[41]

$$V(\rho) = -D_e(1 + \sum_{i=1}^n a_i \rho^i) \exp(-a_1 \rho) \quad (18)$$

Usually, satisfactory results can be obtained when n equals 3. In order to get accurate data, the following form of MS function is used[41, 42]

$$V(\rho) = -D_e(1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3) \exp(-a_1 \rho) \quad (19)$$

where $\rho = R - R_e$ is the inter atomic distance, R_e is the equilibrium distance and D_e is the dissociation energy. The quadratic(f_2), cubic(f_3) and quatric(f_4) force constants can be derived by the M-S function and then spectroscopic parameters harmonic frequency (ω_e), anharmonicity factor ($\omega_e \chi_e$) rotational constant(B_e) and vibration-rotation coupling constant (α_e) can be calcu-

lated by the following relations,

$$f_2 = D_e(a_1^2 - 2a_2) \quad (20)$$

$$f_3 = 6D_e(a_1 a_2 - a_3 - \frac{a_1^3}{3}) \quad (21)$$

$$f_4 = D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 \quad (22)$$

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2} \quad (23)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 m c^2}} \quad (24)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left(\frac{f_3 R_e}{3f_2} + 1 \right) \quad (25)$$

$$\omega_e \chi_e = \frac{B_e}{8} \left[-\frac{f_4 R_e^2}{f_2} + 15(1 + \frac{\omega_e \alpha_e}{6B_e^2})^2 \right]. \quad (26)$$

Once these parameters are obtained from the calculation, it is straightforward to calculate the amplification factor for our purpose.

V. RESULT AND DISCUSSION

TABLE I: Spectroscopic parameters derived for the most abundant isotope $^{80}\text{SeD}(\mu = 1.9645891 a.u)$ from Murrel-Sorbie curve fitting with different Dunning's basis set with the Spin-Orbit coupling at equilibrium.

Basis	Electronic State	R_e Å	ω_e cm^{-1}	$\omega_e \chi_e$ cm^{-1}	B_e cm^{-1}	α_e cm^{-1}	A_e cm^{-1}
a-VTZ-DK	$X^2\Pi$	1.4711	1754.20	22.598	3.9621	0.07327	-1759.72
	$^2\Pi_{\frac{3}{2}}$	1.4711	1750.08	22.429	3.9621	0.07360	
	$^2\Pi_{\frac{1}{2}}$	1.4711	1758.64	22.783	3.9621	0.07294	
VQZ-DK	$X^2\Pi$	1.4689	1769.06	22.576	3.9735	0.0724	-1768.01
	$^2\Pi_{\frac{3}{2}}$	1.4689	1764.85	22.402	3.9735	0.0727	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1773.54	22.765	3.9735	0.0721	
a-VQZ-DK	$X^2\Pi$	1.4689	1764.39	22.588	3.9735	0.0732	-1767.81
	$^2\Pi_{\frac{3}{2}}$	1.4689	1760.41	22.426	3.9735	0.0735	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1768.66	22.762	3.9735	0.0728	
V5Z-DK	$X^2\Pi$	1.4689	1766.88	22.441	3.9735	0.0724	-1770.26
	$^2\Pi_{\frac{3}{2}}$	1.4689	1762.79	22.273	3.9735	0.0728	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1771.27	22.623	3.9735	0.0721	
a-V5Z-DK	$X^2\Pi$	1.4689	1765.11	22.442	3.9735	0.0727	-1770.26
	$^2\Pi_{\frac{3}{2}}$	1.4689	1761.11	22.280	3.9735	0.0730	
	$^2\Pi_{\frac{1}{2}}$	1.4689	1769.41	22.618	3.9735	0.0724	
	Electronic State	R_e Å	ν_0^a cm^{-1}	$\omega_e \chi_e$ cm^{-1}	B_e cm^{-1}	α_e cm^{-1}	A_e cm^{-1}
Expt.	$X^2\Pi$	1.4640	1677.05	21.35	4.00310	0.07985	-1762.696
	$^2\Pi_{\frac{3}{2}}$	-	-	-	-	-	
	$^2\Pi_{\frac{1}{2}}$	-	-	-	-	-	

Three lowest states of Selenium Deuteride radical $X^2\Pi$, $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ are least square fitted to the Murrel-Sorbie function to get the parameters a_1, a_2, a_3, R_e and

D_e of the corresponding states. By using the parameters into the respective equations the spectroscopic parameters are evaluated for the most abundant isotopes of Se i.e. ^{80}Se for the SeD molecule with different correlation consistent with Dunning's basis sets. The potential energy surfaces at the MRCI+Q/a-V5Z-DK for the states $X^2\Pi$, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ of SeD are shown in Fig. 1. The plotted potential energy curves are smooth and show no presence of unphysical kinks along the whole surface.

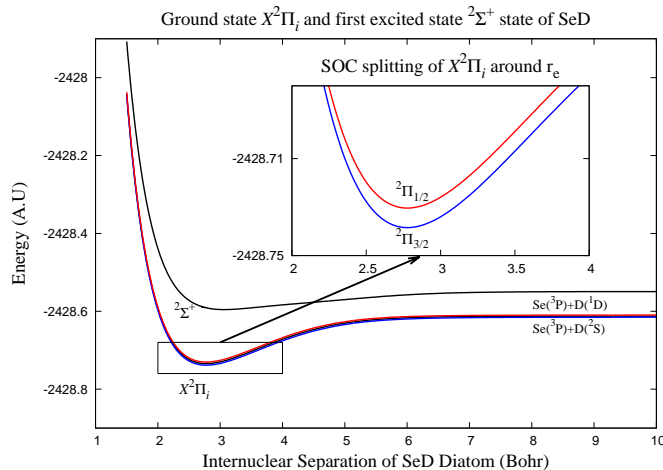


FIG. 1: The PESs of the ground state $X^2\Pi$ and the first excited state $A^2\Sigma^+$ of SeD radical and partly magnified PESs of the states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ near equilibrium (inset) at the MRCI+Q/a-V5Z-DK level of theory.

The variation of spin-orbit energy difference between the two spin orbit components $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ with the change in internuclear separation between Se and D is presented in Fig. 2. This energy interval can be regarded as the vertical transition energy from $X^2\Pi_{3/2}$ to $^2\Pi_{1/2}$ which is determined by the SOC splitting of the ground electronic state $X^2\Pi$. Increasing the inter-atomic separation from the equilibrium distance 2.776 a.u., the curve exhibits a little increase (12 cm^{-1}) upto 3.56 a.u. and then a gradual decrease is observed to about 1207.91 cm^{-1} at 10 a.u. The curve shows the SOC between $X^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ is lower than 1780 cm^{-1} at all inter nuclear separation which supports the perturbative treatment of SOC in this case.

Relevant spectroscopic parameters such as, harmonic frequency ω_e , anharmonicity factor ($\omega_e\chi_e$), rotational constant (B_e) and vibration-rotation coupling constant (α_e) along with equilibrium bond length and Spin-Orbit Coupling (SOC) are tabulated with different electron correlation consistent Dunning's basis set in Tab. I.

It is evident from Table I that the predicted equilibrium bond lengths of SeD using MRCI at different basis sets reveal almost no discernible variation from quadruple zeta quality basis sets to quintuple zeta basis sets and is less than 0.0001\AA . The estimated R_e is also in excellent

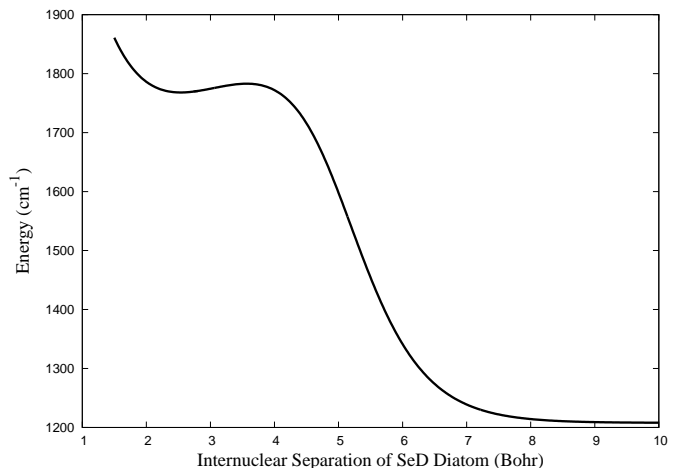


FIG. 2: The curve for the vertical transition energy of SeD $X^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$ transition energy (cm^{-1}) vs. the internuclear separation at MRCI+Q/a-V5Z-DK level of theory.

agreement with the previously measured bond lengths of SeD (1.4640\AA) from Laser Magnetic Resonance based experiments [21]. We find the deviation at MRCI/a-V5Z-DK is less than 0.005\AA . Moreover, the estimated spectroscopic constants, also show excellent convergence at better quality basis sets. In general theoretically estimated spectroscopic constants also exhibit excellent agreement with the experimentally determined values. However for ω_e , we find that the agreement between the experimental and theoretical value can be termed satisfactory at best. Decades back Brown and co-workers have determined the band origin of SeD vibrational spectrum to be 1677.05 cm^{-1} [21]. Using the equation $\nu_0 = \omega_e - 2\omega_e\chi_e$, where ν_0 is the fundamental vibrational band origin the ω_e is estimated to be 1719.75 cm^{-1} [21]. On the contrary the ω_e predicted from the Murrell-Sorbie fit to the MRCI potential energy surface predicts a ω_e of 1765.11 cm^{-1} . Harmonic frequency derived numerically by determining the 2nd derivative of energy with respect to nuclei displacement about the equilibrium geometry is predicted to be 1712.12 cm^{-1} . We have checked also the ω_e with other reliable electronic structure methods such as coupled cluster singles and doubles (CCSD) [43–45] and coupled cluster singles and doubles with perturbative Triples corrections (CCSD(T)) [46] with electron correlation consistent Dunning's basis sets. These methods can provide accurate estimates for harmonic frequencies (ω_e) as at equilibrium bond length if the system under consideration can be well approximated through a single determinant wavefunction. All of these values for harmonic frequencies are reported in Table II. The amplification factor, K is dependent on the harmonic frequency. Hence using different harmonic frequencies we get a wide ranging spread for the amplification factor as shown in Table II. The amplification factor can be as high as 1070. If use only theoretical estimates the maximum amplification factor

can be 350. On the lower side it can be 34. Even if we consider the lowest amplification factor one can safely conclude that this molecule can be an effective probe for measuring space time variation of fundamental constants.

TABLE II: Amplification factor(K) predicted at different level of theory with the experimental SOC

Isotope	Electronic State	Level of Theory	ω_e^a cm^{-1}	A_e or ω_f^b cm^{-1}	Amplification factor(K) $K = \frac{\omega_f}{\omega_f - v\omega_e}$
^{80}SeD	$^2\Pi$	CCSD/a-VQZ-DK	1761.04	-1762.696	1064.42
^{80}SeD	$^2\Pi$	CCSD(T)/a-VQZ-DK	1738.05	-1762.696	71.52
^{80}SeD	$^2\Pi$	MRCI/a-VQZ-DK	1712.12	-1762.696	34.85
^{80}SeD	$^2\Pi$	Expt.[21]	1719.75	-1762.696	41.04

Since from the above table, the spin-orbit coupling constant A_e and harmonic frequency ω_e are very similar in magnitude for SeD radical in its ground state electronic multiplet $X^2\Pi_i$, $G(v+1)^{\frac{3}{2}}$ is quasi-degenerate with $G(v)^{\frac{1}{2}}$ level for $v = 0, 1, 2, 3, \dots$. As mentioned in the introduction, for measuring space-time variation of fundamental physical constants, we have to have a large value of amplification factor (K) for the transition between quasi-degenerate vibronic levels. The energy difference between the quasi-degenerate vibronic levels can be expressed as,

$$\begin{aligned}\Delta G(v) &\equiv G(v)^{\frac{1}{2}} - G(v+1)^{\frac{3}{2}}, \\ &= -A_e - \omega_e + 2B_e - 2\alpha_e \\ &\quad + (2\omega_e\chi_e + \alpha_{A_e})(v+1)\end{aligned}\quad (27)$$

For the most abundant four isotopes of SeD at the MRCI+Q/a-V5Z-DK level of theory, the change of $\Delta G(v)$ is tabulated in Table III. $\Delta G(v)$ is positive for all vibrational levels and increases with the vibrational quantum number due to anharmonicity. For $v = 0$ the vibrational levels of the two states become closest to each other.

TABLE III: Difference between quasi-degenerate vibronic states for the four most abundant isotope SeD with increasing vibrational quantum number.

Isotope	$\Delta G(v)$ cm^{-1}	$\Delta G(v=0)$ cm^{-1}	$\Delta G(v=1)$ cm^{-1}	$\Delta G(v=2)$ cm^{-1}
^{77}SeD	$11.85+36.62(v+1)$	48.47	85.09	121.71
^{79}SeD	$12.54+36.59(v+1)$	49.13	85.72	122.31
^{80}SeD	$12.84+35.58(v+1)$	49.40	83.98	119.57
^{82}SeD	$13.34+35.58(v+1)$	49.89	86.44	122.99

Since for $v = 0$ the vibrational levels of the two states come within a 50 cm^{-1} , rotational states with J -value from the two states interact significantly with each other. Rotational energies of both the doublet states are expressed with the same expression i.e. $F_v(J)^{(\frac{1}{2})} =$

$F_v(J)^{(\frac{3}{2})} = B_e[J(J+1) - \alpha_e J(J+1)(v + \frac{1}{2})]$. Therefore the energy associated with the microwave transition is $\Delta F_v(J) = F_v(J)^{(\frac{1}{2})} - F_v(J)^{(\frac{3}{2})}$. Now the selection rule for microwave transition is $\Delta F_v(J) = \pm 1$ i.e. $\Delta L + \Delta J = \pm 1$, which leads to two possibilities, one is $\Delta L = \pm 1, \Delta J = 0$ (only observed for open shell molecule which leads to Q-Branch spectra) and another is $\Delta L = 0, \Delta J = \pm 1$ (Which leads to P and R-Branch spectra). So the overall selection rule for this kind of doublet species is $\Delta J = 0, \pm 1$. For $\Delta J = 0$ transitions, there are no change in the rotational energy. So we are considering only those transitions which follow the selection rule $\Delta J = \pm 1$. For $\Delta J = +1$, $\Delta F_{v=1}(J) = 2B_e(J+1) - \alpha_e J(J+1)(J+3)$ and for $\Delta J = -1$, $\Delta F_{v=1}(J) = -2B_e J - \alpha_e J(J-2)$.

Now the transitions of interest are those which lead to $\Delta E(v, J) \approx 0$ i.e. $\Delta G(v) + \Delta F_v(J) \approx 0$. Since for $v = 1$ vibronic levels of the two doublet states come closest and $\Delta G(v=0)$ is a positive quantity ΔJ have to be -1. Therefore $\Delta G(v=0) + \Delta F_v(J) \approx 0$.

$$\begin{aligned}\Delta G(v=0) &= -\Delta F_v(J), \\ &= -(-2B_e J - \alpha_e J(J-2)), \\ &= 2B_e J + \alpha_e J(J-2)\end{aligned}\quad (28)$$

From the table of the spectroscopic parameters we notice the fact that $\alpha_e \ll B_e$ in magnitude and we neglect the term containing α_e to convert the equation into linear equation $\Delta G(v=0) = 2B_e J$ and solve for J leading to

$$J = \frac{\Delta G(v=0)}{2B_e} = 6.21 \approx 6$$

For open shell systems J is essentially half integer, the two appropriate choices of J be $J = 6\frac{1}{2}$ and $J = 5\frac{1}{2}$.

A. Variation of ro-vibronic transition frequency with respect to variations of α and μ :

The ro-vibrational energy difference between two electronic states can be expressed as,

$$\begin{aligned}\Delta E_v(J) &= \Delta G(v) + \Delta F_v(J), \\ &= A_e - \omega_e - \alpha_e + 2B_e + \\ &\quad v(2\omega_e\chi_e - \alpha_{A_e}) - 2B_e J - \alpha_e J(J-2)\end{aligned}\quad (29)$$

So for the variation in energy difference $\Delta E_v(J)$ in terms of variation in α and μ can be expressed as,

$$\delta E_v(J) = \delta(A_e - \omega_e - \alpha_e + 2B_e + \quad (30)$$

$$\begin{aligned}&\quad v(2\omega_e\chi_e - \alpha_{A_e}) - 2B_e J - \alpha_e J(J-2)), \\ &= \delta(A_e - \omega_e)\end{aligned}\quad (31)$$

As other terms are negligible compared to A_e and ω_e they are neglected in equation (30). Now the spin-orbit constant A_e varies as $\sim Z^2\alpha^2 E_H$ and ω varies as

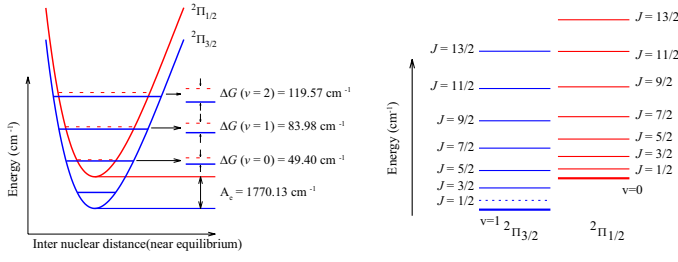


FIG. 3: (left) The magnitude of Vibronic levels of the two doublet states of ^{80}SeD . The blue lines represents $^2\Pi_{3/2}$ and red line represents $^2\Pi_{1/2}$ MRCI+Q/a-V5Z-DK level of theory. (right) Rotational levels of the two doublet states. The blue (solid) lines represents $^2\Pi_{3/2}$ and red (dashed) line represents $^2\Pi_{1/2}$. Since J is always $\geq \Omega$ so for $^2\Pi_{3/2}$, $J = \frac{1}{2}$ rotational level is not observed.

$M_r^{-\frac{1}{2}} \mu^{-\frac{1}{2}} E_H$ as mentioned in the introduction so overall variation in transition energy will be,

$$\begin{aligned} \delta E_v(J) &= \delta(A_e - \omega_e), \\ &\cong 2A_e \left(\frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right), \\ &= 3540 \text{ cm}^{-1} \left(\frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right) \end{aligned} \quad (32)$$

For SeD the values are shown in Fig. 3. Therefore a large enhancement factor may be obtained by proper choice of a molecular probe, in this case the SeD radical which is likely to be found under certain astrophysical conditions like an AGB star.

VI. CONCLUSION

To summarize, for SeD molecule, we have analyzed the sensitivity of the ro-vibronic spectrum to variations in the fundamental physical constants. We have found enhanced sensitivity for a number of low frequency microwave transition within $^2\Pi_{1/2}(v=0)$ and $^2\Pi_{3/2}(v=1)$ which may enhance the amplification factor upto the order of ~ 350 . We acknowledge the fact that the data produced in the calculation should not be considered as accurate as microwave frequency because the error bar of the MRCISD+Q level of theory can be as large as $\sim 100 \text{ cm}^{-1}$. Fairly accurate data can only be obtained from high precision laboratory experiments. So, experimental evidence is necessary on the molecule to confirm our findings.

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